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## PATENT SPECIFICATION

(11) 1517 341 ✓

1517 341

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 (72) Inventors JOHN ALLAN TOPPING and WILLIAM EDWIN MOSS

(19)



#1

SOIN. FORMING TRANSPARENT, INFRARED REFLECTIVE, CONDUCTIVE  
 COATINGS + SP. USEFUL FOR GLASS OVEN WINDOWS  
 (54) COATING SOLUTIONS FOR DIELECTRIC MATERIALS

- (71) We, DAY SPECIALTIES COMPANY LIMITED, a company organized under the laws of the Province of Ontario, of 125 Albert Street, Midland, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to coating solutions for the production of conductive, transparent and infra-red reflective coatings on dielectric materials, typically glass, ceramics or other high temperature insulating materials.
- 15 Conductive, transparent and infra-red (or heat) reflective films based on tin oxide are well known. Such films typically have been formed by thermal decomposition of a tin salt, such as stannic chloride on a heated surface of the dielectric material, the tin salt typically being applied as an aqueous solution.
- 20 One particular application of heat reflective films is in oven door windows. Regulations exist governing the maximum external temperature of such ovens and are becoming more stringent.
- 25 Additionally, it is preferred to have at least an inner pane of the oven door window formed of tempered glass. Application of the tin oxide film to tempered glass usually results in loss of temper on heating the glass for application of the thermally decomposable tin salt. Attempts at tempering tin oxide coated glass sheets usually lead to cracking of the sheets due to thermal stresses introduced by the presence of the tin oxide film.
- 30 The present invention allows the provision of a tin oxide coating on glass or other dielectric material which is transparent and conductive and has improved heat reflective properties. By the present invention it is possible to provide a coated glass sheet conforming to the more stringent regulations mentioned above, which glass sheet can be tempered.
- 35 According to the present invention there is provided a solution which consists solely of at least one polar solvent having dissolved therein
- (a) a tin salt which is thermally decomposable to form a transparent oxygen-deficient tin oxide coating film on the surface of a substrate; 50
- (b) at least one dopant selected from  $\text{PCl}_5$ ,  $\text{SbCl}_5$ ,  $\text{SbF}_5$ ,  $\text{InCl}_3$ ,  $\text{HF}$ ,  $\text{AlCl}_3$ ,  $\text{GaCl}_3$  and  $\text{BiCl}_3$ , the dopant being present in a quantity sufficient to reduce the surface resistivity of such a tin oxide film to less than 500 ohms per square and to increase the infra-red reflectance of such a film; and, optionally, 55
- (c) an organic reducing agent. 60
- Pure stoichiometric tin oxide ( $\text{SnO}_2$ ) is an insulator and will not reflect infra-red radiation appreciably. However, tin oxide (i.e.  $\text{SnO}_{2-x}$ ) formed by thermal decomposition of thermally-decomposable salts of tin is usually oxygen deficient and an n-type semi-conductor the excess tin acting as donor providing an increased density of electrons in the conduction band. 65
- In accordance with the present invention, the conductivity and the infra-red reflectance of a tin oxide coating film are improved by use of the dopant, which functions by replacement of  $\text{Sn}^{4+}$  by  $\text{In}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Sb}^{3+}$  or  $\text{P}^{3+}$ , and/or  $\text{O}^{2-}$  by  $\text{F}^-$  or  $\text{Cl}^-$ . Preferred dopants are  $\text{SbCl}_5$ ,  $\text{SbF}_5$  and  $\text{HF}$ . 70
- The concentration of dopant used in the solution depends on a number of factors, including the type and chemical nature of the dopant and the end use for the coated glass sheet. 75
- The polar solvent may be wholly water, wholly an organic polar solvent or a mixture of water and organic polar solvents. Typical examples of organic polar solvents are ethers, such as diethyl ether, aldehydes such as acetaldehyde, ketones, such as acetone, methyl ethyl ketone and diethyl ketone, carboxylic acids, such as formic acid and acetic acid, esters, such as methyl formate, methyl acetate and butyl acetate, and alcohols, such as methanol and ethanol. Mixtures of such polar solvents may be used. 80
- While such materials generally are unnecessary, 85
- 90

sary to provide the desired heat-reflecting properties, sugars, starch, celluloses and other similar organic reducing agents may be present in the solution spray applied to the substrate.

5 The solution used in this invention is capable of forming oxygen-deficient tin oxide coating films on both small and large objects and, in the case of the large objects, such as large  
10 area glass sheets, the electrical resistance of the coating is substantially uniform over the area of the coating, unless the coating is deliberately formed to have varying electrical properties.

15 The solutions according to the present invention are particularly useful for the coating of oven door windows and will be described with particular reference thereto. However, they may be used for coating the surface of  
20 other dielectric substrates for use as heat mirrors in other applications, for example, in building windows and in solar energy collection systems. The coated dielectric substances also may be used to provide electric heaters  
25 in windshields in automobiles, aircraft and the like for demisting or deicing, and in high power line insulations to prevent condensation thereon, or used as transparent electrodes, typically for use in optical display systems  
30 such as liquid crystals.

The dielectric substrate on which the coating is formed in accordance with the present invention is preferably glass, typically in sheet form. However, in certain applications, dielectric materials other than glass may be used,  
35 such as ceramic and other high temperature insulating materials.

The glass may be of any suitable composition which may be heated without undue deformation to the required temperature for formation of the metal oxide film thereon. A common commercially-available glass which is suitable is soda-lime-glass, obtainable in sheet  
40 glass, plate glass and float glass forms. Tinted soda-lime glasses, such as bronze glass and solar cool, also may be used. Other glasses which may be used include soda borosilicate glasses (for example, "Pyrex" — Pyrex is a Trade Mark), soda aluminosilicate glasses,  
45 fused silica and fused quartz.

50 The temperature to which the glass is required to be heated when applying solutions according to the present invention depends on the glass composition, the heat capacity of the glass sheet, thicker sheets having a higher heat capacity than thinner sheets, and the nature of the film-forming composition applied to the glass sheet. In any case, however, a temperature in the range of 350° to 800°C is used.

55 The coating is preferably applied to the glass sheet by spraying the solution according to the invention onto the glass surface.

60 The solution is sprayed, preferably as a mist, to allow ready evaporation of solvent, onto the surface to be coated, generally applying the  
65

spray evenly to the surface, although uneven application may be desired in some instances. Although a single spray application often may be used to provide the desired thickness of oxide coating upon thermal decomposition of the metal salt, it is preferred to apply the solution in a multiple number of sprayings, allowing the heat sink of the body of the glass sheet to heat up the surface close to its original temperature between sprayings, typically allowing about a one-second gap between sprayings. Procedure in the latter manner results in more efficient heat utilization.

The coatings produced according to this invention exhibit the property of reflecting long-wave infra-red heat over a wide temperature range. The coatings also are transparent by which we mean that the coated sheets exhibit visible light transmission.

The heat-reflecting properties of the coating formed from solutions according to the invention are related to the electrical resistance of the coating, the relationship varying for varying dopants and solvents. In general, the lower the electrical resistance of the coating, the greater is the heat reflecting property of the coated sheet.

The electrical resistance of the coating in turn is controlled by the type of dopant, concentrations of the dopant based on the tin salt, and the thickness of the coating on the substrate. These parameters are varied to provide an electrical resistance below 500 ohms, typically in the range 50 to 300 ohms, and at these electrical resistances good heat reflecting properties are obtainable. Typically, the thickness of the coating is between about 10 and 50 microinches.

The dopant is dissolved in a tin chloride solution to be sprayed onto the hot glass surface for formation of the semi-conductive tin oxide coating.

It has been found that a glass sheet coated on both surfaces with a solution according to the invention can be tempered without stress cracking; such tempering results in improved overall heat reflecting performance of the glass sheet compared with an untempered double coated glass sheet. A tempered glass sheet having an electrically conductive transparent tin oxide film on both faces thereof, each tin oxide film having a surface resistivity of less than 500 ohms per square is described and claimed in our Divisional application No. 52561/77.

The provision of a tin oxide coating on both faces of glass sheet in accordance with the invention has additional advantages to that of the ability to temper the glass sheet. Thus, the heat reflectance of the glass sheet is improved by the second heat mirror as compared to an equivalent sheet having only one face coated. The double coated sheet has the surprising property of less heat transmission than two single coated sheets in a double-glazed oven door window.

Oven door windows generally consist of two or more spaced and parallel glass sheets. The single or double coated sheet provided in accordance with this invention is used as the inner sheet. The heat passage inhibiting properties of the window may be improved further by the application of a metal film, such as platinum, over the inner surface of the outer sheet. To allow for visibility through the window, such metal film typically is applied to give partial coverage of the glass, for example, in a cross-hatch manner. Such oven door window assemblies are described and claimed in our Divisional Application No. 52561/77.

The ability of the heat reflective tin oxide coated glass sheets provided in the present invention, when used in domestic oven door windows to reflect radiant heat from inside the oven back into the oven, results in a number of advantages, as compared with the uncoated window. Thus, the temperature of the outer surface of the door is decreased, thereby rendering the outer surface safer to touch by hand, particularly by small children. Further, since less heat is lost from the oven, less heat need

be produced by the heating elements or gas burners, thereby resulting in a lower energy utilization. Additionally, since less heat is lost through the window, the temperature gradient in the oven is decreased and this leads to more even heating and hence more even cooking.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only.

In the Examples, reference will be made to the accompanying drawings, in which:

Figures 1 to 3 are infra-red spectra of glass sheets coated with tin oxide films formed from solutions in accordance with the invention; and

Figure 4 is a graphical representation of the variation in external temperature of three oven windows with internal temperature of the oven comparing windows coated in accordance with the present invention and prior art.

#### Examples 1 to 13.

A number of solutions for spraying on to heated glass sheet samples measuring 6" x 3½" were prepared. The solutions had the compositions set forth in the following Table I:

TABLE I

Solution	Tin Salt	Quantity gms.	Dopant	Quantity	Solvent	Organic Reducing agent	Quantity gms.
A	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	105	None	None	water 4mls Ethanol 7mls	Dextrose	2
B	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	105	HF	4.16mls (52%)	water 3.78mls Ethanol 7mls	Dextrose	2
C	$\text{SnCl}_4$	22.5	HF	1.95mls	water 17.8mls Ethanol 6.9mls	Dextrose	0.6
D	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	67.3	HF	1.95mls	water 1.2mls Ethanol 6.9mls	Dextrose	0.6
E	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	67.3	HF	1.95mls	water 1.2mls Ethanol 6.9mls	—	—
F	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	67.3	HF	1.95mls	water 1.2mls	—	—
G	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	132.15	$\text{SbCl}_3$	1.311gms	water 2.45mls methanol 13.75mls	—	—
H	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	130.2	$\text{SbCl}_3$	2.62gms	water 2.45mls methanol 13.75mls	—	—
I	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	126.18	$\text{SbCl}_3$	5.24gms	water 2.45mls methanol 13.75mls	—	—
J	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	131.55	$\text{InCl}_3 \cdot 3\text{H}_2\text{O}$	2.11gms	water 2.04mls methanol 13.75mls	—	—
K	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	131.55	HF	3.9mls (52%)	water 2.04mls methanol 13.75mls	Dextrose	1.3

Utilizing the compositions outlined in the above Table I, glass sheets were sprayed after preheating to 650°C in a vertical furnace to provide, in most cases, a single coated sheet, although in some cases a double coated sheet was provided. In each instance the resistance of the coating was measured and in some cases

infra-red spectra were recorded. Such spectra appear as Figures 1 to 3 of the accompanying drawings.

The conditions employed and the results obtained are reproduced in the following Table II:

TABLE II

Example No.	Solution used	No. of Sprays	Time for each spray (secs.)	Single (S)	Double (D)	Resistance of coating (ohms)	IR Spectrum no.
1	A	7	2	S	—	250	1
2	B	8	3	S	—	30 to 40	2
3	C	6	3	—	D	S1-56 S2-64	3
4	D	6	3	—	D	S1-24 S2-20	4
5	E	7	3	S	—	45	—
6	E	7	3	S	—	44	—
7	E	8	3	S	—	32	5
8	F	6	3	S	—	60	6
9	G	6	3	S	—	37	7
10	H	8	3	S	—	68	—
11	I	8	3	S	—	110	—
12	J	8	3	S	—	60	8
13	K	6	3	S	—	46	—

5 The results reproduced in the above Table II and shown in the accompanying infra-red spectra illustrate the production of conductive infra-red reflective coatings and the superiority of utilizing a dopant in the composition may be seen by comparing the result obtained by the use of the composition A as compared with the other compositions.

Example 14.  
The double coated glass sheet of Example 3 was subjected to tempering and the resistance of the tempered sample was measured. The results are reproduced in the following Table III:

TABLE III

Example No.	Resistance (ohms)			
	Before Tempering Side 1	Before Tempering Side 2	After Tempering Side 1	After Tempering Side 2
3	56	64	45	55

20 Taking a decreased resistance as indicating an improved infra-red reflectance, the results of the above Table III indicate an improved infra-red reflectance on tempering for the sample of Example 3.

#### Example 15.

25 A plurality of glass sheets were tested as the inner panel of a double glazed oven door window assembly in a test oven. One sample (A) was a conventional uncoated soda-lime glass sheet, one sample (B) was a commercially-

available heat reflective glass sheet and one sample (C) was a double coated glass sheet provided in accordance with Example 4. The external temperature of the double glazed window assembly for each of the three samples was measured for various internal temperatures of the oven. External temperatures were measured by means of an indicating potentiometer and a chromed Alumel (Alumel is a Trade Mark) thermocouple. The thermocouple was brought through a copper disc of 0.024 inch thickness and 7/32 inch diameter and brazed

so that the temperature measuring face was smooth and flat. The lead wires from the junction were 24 Asg.

- 5 The results for the three samples were plotted as a graph and the graph appears as Figure 4 of the accompanying drawings. As may clearly be seen from the graph, the commercially-available sample (B) was an improvement on the uncoated sample (A) but the
- 10 sample (C) provided in accordance with the present invention was a significant improvement on the sample (B).

#### Examples 16 to 31.

A G.E. Self-Clean 1974 model stove was set up with a 7" x 16" double-glazed glass window in the oven and several glass sheets, coated on a single side with tin oxide films using solutions according to the invention and generally following the procedure of Examples 1 to 13, were installed as the inner glass sheet of the window. In each case, the oven was set at an internal temperature of 450°F and the outer temperature was measured. A comparative test was carried out on the existing window. The results are reproduced in the following Table IV:

TABLE IV

Example No.	Compositions Parts by Weight		Solvent	Solvent	Surface Resistance ohms	Outer Surface Temperature °F
	SnCl <sub>4</sub> .5H <sub>2</sub> O	SbCl <sub>3</sub>				
16	Existing window—Plain Glass		—	—	—	130
17	30	0.3	70	Ethanol	500 to 1000	124
18	90	0.9	10	Ethanol	50 to 100	113
19	30	0.3	70	Water	250 to 500	126
20	90	0.9	10	Water	40 to 60	124
21	10	0.1	90	Butyl Acetate	2500 to 3200	124
22	30	0.3	70	Butyl Acetate	80 to 150	122
23	90	0.9	10	Butyl Acetate	70 to 140	115
24	30	0.3	70	Formic Acid	300 to 800	119
25	90	0.9	10	Formic Acid	100 to 180	116
26	10	0.1	90	Methyl Ethyl Ketone	700 to 1100	120
27	30	0.3	70	Methyl Ethyl Ketone	70 to 110	111
28	90	0.9	10	Methyl Ethyl Ketone	100 to 150	116
29	30	0.3 (AlCl <sub>3</sub> )	70	Methyl Ethyl Ketone	170 to 370	123
30	10	0.1	90	Diethyl Ether	1.5 to 2.0K	119
31	30	0.3	70	Diethyl Ether	60 to 120	113

- 30 The results of the above Table IV show that in each case using the tin oxide coated glass sheets, there was an improvement (lowering) of the outer temperature of the oven window, in some cases by 10 to 15°F or more. In each case, for a particular combination of dopant and solvent, the outer temperature decreased with decreasing film resistance.
- 35

#### Example 32.

Further oven tests were carried out in the same manner as in Examples 16 to 31, except

that, in this case, the outer pane of the double oven window was provided with a cross-hatched platinum coating over about 75% of the surface while the inner window was a double coated pane provided from solution G of Table I and having coatings of resistance 20 to 70 ohms. Tests were carried out with the platinum coating facing inwardly and outwardly at an internal oven temperature of 450°F. The results are reproduced in the following Table V:

40

45

TABLE V.

Facing Direction of/ Pt cross-hatch	Outer Temperature °F
No cross-hatch	105
Inwardly	99
Outwardly	110

The results of this Table V show that the

direction of facing of a cross-hatched outer sheet is significant in determining the outer surface temperature.

## Example 33.

The energy utilization of the commercial oven mentioned in Examples 16 to 31 when various oven windows are installed was determined and the results are reproduced in the following Table VI:

TABLE VI

Window	Total Test Time	Total Power Used (Kw)	Energy used /hr.	% Energy Change
Outer plain glass Inner glass-Double coated as Example 32	25	18.85	0.72 KWH	+9% Saving
Outer plain glass Inner Glass-Same as commercial material of (B) of Example 15	20	15.2	0.73 KWH	+7.5% Saving
Outer and inner plain glass.	24.05	19.56	0.79 KWH	-
Outer and inner plain glass with forced air passing between panes	18.75	16.28	0.825 KWH	-12% loss

The results of the above Table VI illustrate the energy conservation attainable using the glass sheets coated from solutions provided by the invention and the superiority of such sheets over the commercially-available product.

## WHAT WE CLAIM IS:—

1. A solution which consists solely of at least one polar solvent having dissolved therein (a) a tin salt which is thermally decomposable to form a transparent oxygen-deficient tin oxide coating film on the surface of a substrate;
- (b) at least one dopant selected from  $\text{PCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{SbF}_3$ ,  $\text{InCl}_3$ ,  $\text{HF}$ ,  $\text{AlCl}_3$ ,  $\text{GaCl}_3$  and  $\text{BiCl}_3$ , the dopant being present in a quantity sufficient to reduce the surface resistivity of such a tin oxide film to less than 500 ohms per square and to increase the infra-red reflectance of such a film; (c) an organic reducing agent.
2. A solution according to claim 1, in which the polar solvent comprises an ether, an aldehyde, a ketone, a carboxylic acid, an ester or an alcohol.
3. A solution according to claim 1 or 2, in which the polar solvent comprises water.
4. A solution according to claim 3, in which the polar solvent is a mixture of water and an alcohol.
5. A solution according to any of claims 1

to 4, in which the tin salt is stannic chloride.

6. A solution according to any of claims 1 to 5, in which the dopant is  $\text{HF}$ ,  $\text{SbF}_3$ , or  $\text{SbCl}_3$ .

7. A solution according to claim 1, substantially as herein described in any of Solutions B to K in Table I or in any of Examples 17 to 31.

8. A method of coating a surface of a dielectric substrate, which comprises spraying a solution according to any of claims 1 to 7 on to the surface, which surface has been heated to a temperature which is above the decomposition temperature of the tin salt and which is in the range  $350^\circ\text{C}$  to  $800^\circ\text{C}$ , whereby the tin salt is oxidatively decomposed to produce the transparent oxygen-deficient tin oxide coating film on the substrate.

9. A method according to claim 8, in which the spray is applied in the form of a mist.

10. A method according to claim 8 or 9, in which the substrate is a glass sheet.

11. A method according to claim 10, in which a coating film is produced on both faces of the sheet.

12. A method according to claim 10 or 11, further comprising the step of tempering the glass sheet after production of the coating film(s).

13. A method according to claim 8, substantially as herein described in any of Examples 2 to 13 or 17 to 31.

*Solvent  
Spraying  
Technique*

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1517341

COMPLETE SPECIFICATION

3 SHEETS

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Sheet 1

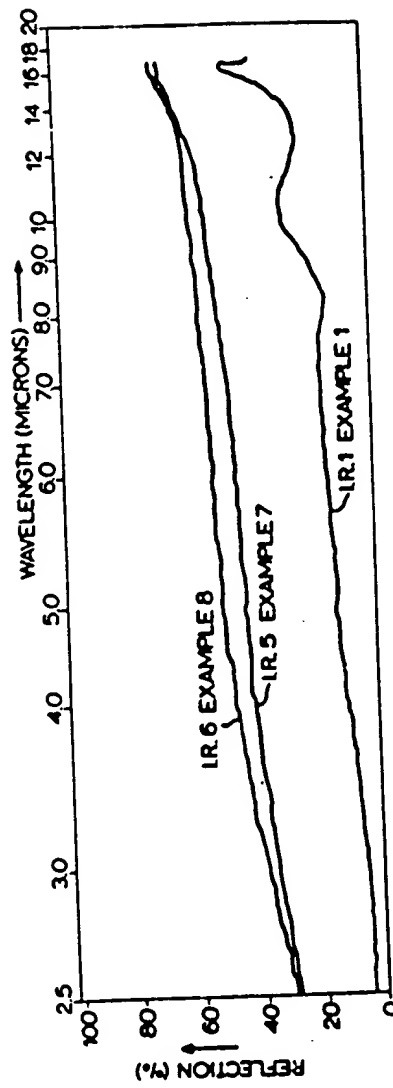


FIG. 1

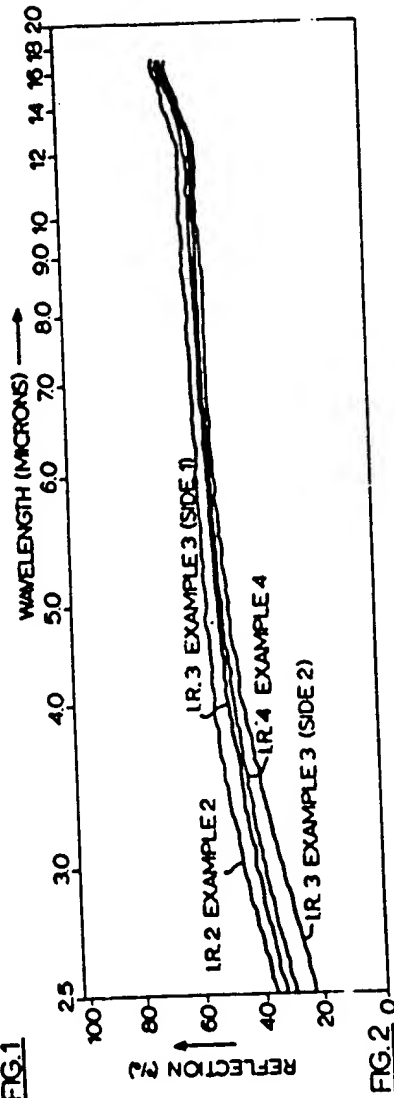


FIG. 2

1517341

COMPLETE SPECIFICATION

3 SHEETS

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the Original on a reduced scale*

Sheet 2

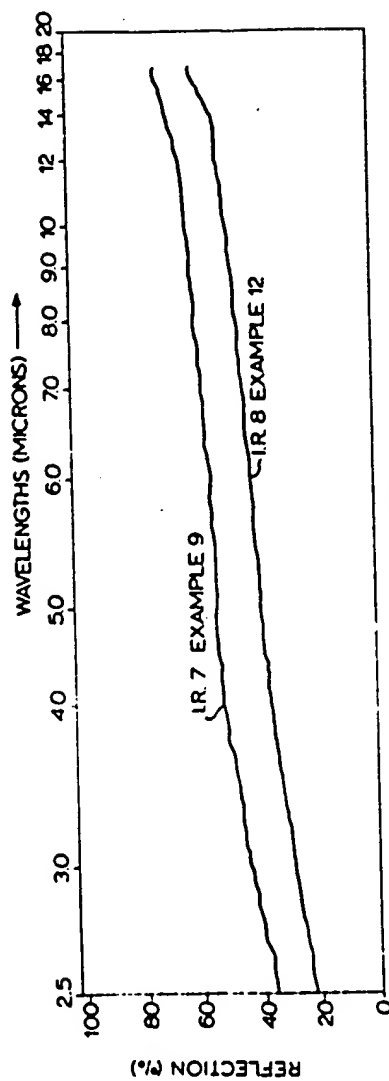


FIG. 3

1517341

COMPLETE SPECIFICATION

3 SHEETS

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Sheet 2

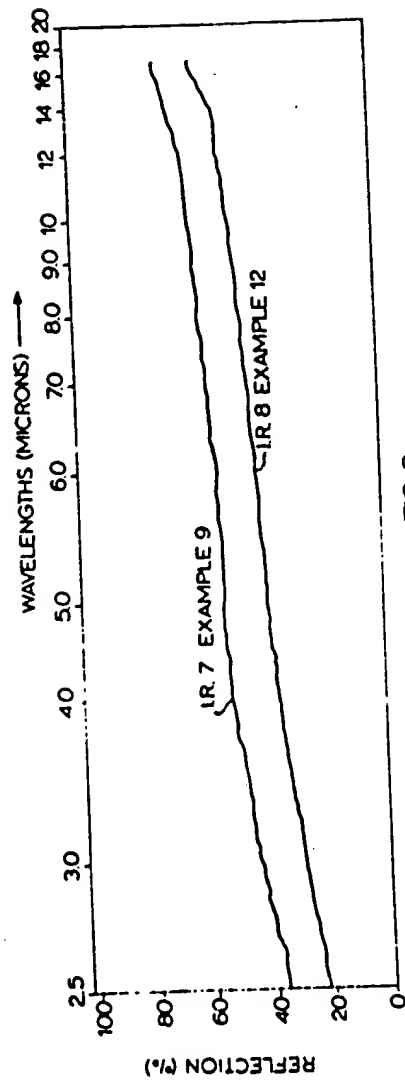


FIG. 3

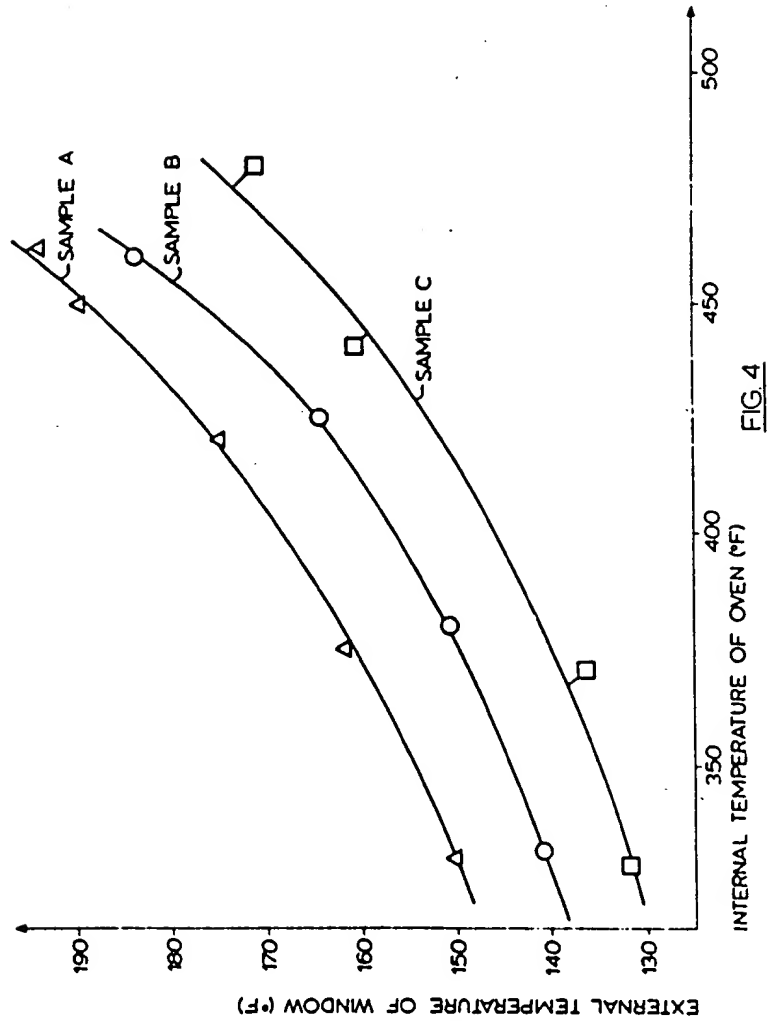


FIG. 4

5/5/27 (Item 13 from file: 351)  
DIALOG(R)File 351:DERWENT WPI  
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008665038 WPI Acc No: 91-169065/23  
XRAM Acc No: C91-073291

Mfg. near-IR cutting glass for buildings or vehicles - by spraying aq.  
soln. of butyl-tin trichloride, antimony trichloride, and lower alcohol  
or xylene onto glass plate surface, etc.

Patent Assignee: (NIPG) NIPPON SHEET GLASS KK

Number of Patents: 001

Patent Family:

CC Number	Kind	Date	Week
JP 3103341	A	910430	9123 (Basic)

Priority Data (CC No Date): JP 89239294 (890914)

103 341/91.

239 247/84.

Abstract (Basic): JP 3103341

A process for mfg. a near-IR cutting glass which comprises a glass plate having deposited thereon a thin film contg. 60-87.5% SnO<sub>2</sub> and 12.5-40% Sb<sub>2</sub>O<sub>3</sub>, having a visible ray transmittance of 5-35%, a solar radiation transmittance of 15-45% and a diffusion transmittance of visible rays of 2% or less, comprises: spraying a mixed soln. of C<sub>4</sub>H<sub>9</sub>SnCl<sub>3</sub>, SbCl<sub>3</sub>, H<sub>2</sub>O, and C<sub>n</sub>H(2n+2)OH (n = 1-3) or C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> onto the surface of glass plate heated to a high temp., to thereby form the SnO<sub>2</sub> and Sb<sub>2</sub>O<sub>3</sub> based thin film by pyrolysis of the mixed soln.

The mixed soln pref. contains Sb(CH<sub>3</sub>COO)<sub>3</sub> in the place of SbCl<sub>3</sub>; otherwise, the mixed soln. comprises C<sub>4</sub>H<sub>9</sub>SnCl<sub>3</sub>, SbCl<sub>3</sub>, CH<sub>3</sub>OH, and H<sub>2</sub>O (10 wt.% or less w.r.t. methanol); or the mixed soln. comprises C<sub>4</sub>H<sub>9</sub>SnCl<sub>3</sub>, SbCl<sub>3</sub> or Sb(CH<sub>3</sub>COO)<sub>3</sub>, and CH<sub>3</sub>OH.

USE/ADVANTAGE - Provides near-IR cutting glass for use in buildings and in motor cars. @ (5pp Dwg.No.0/4)@

File Segment: CPI

Derwent Class: L01;

Int Pat Class: C01G-030/00; C03C-017/25

Manual Codes (CPI/A-N): L01-G04D; L01-L01; L01-L02; L01-L05

$$\left[ \frac{\text{Sb}}{\text{Sn}} \right] \text{molar} = 0.148 - 0.688$$

$$\text{Amu} \rightarrow 0.01 - 0.5$$

$$\text{mols. of rtf.} \cdot 0.06$$

$$\text{Best range} \cdot 0.01 - .15$$

Limit range to below 0.148

See Ex. 15

$$\text{Pl. 5} \cdot 0.01 - .12$$

$$0.14$$

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XP 000318066

C03C17/25 B

M03C17 8110

M03C17 8211

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115: 141095q Manufacture of glass for shielding of near-infrared. Fujisawa, Akira; Misonoo, Masao; Hirata, Masahiro; Kawahara, Hideo (Nippon Sheet Glass Co., Ltd.) Jpn. Kokai Tokkyo Koho JP 03,103,341 [91,103,341] (Cl. C03C17/25), 30 Apr 1991, Appl. 89/239,294, 14 Sep 1989; 5 pp. Glass plates are coated with mixt. contg. 60-87.5% SnO<sub>2</sub> and 12.5-40% Sb<sub>2</sub>O<sub>3</sub> by thermolytic oxidn. of mixts. contg. C<sub>4</sub>H<sub>9</sub>SnCl<sub>3</sub>, SbCl<sub>3</sub> or Sb(OAc)<sub>3</sub>, H<sub>2</sub>O, and C<sub>n</sub>H<sub>2n+1</sub>OH (n = 1-3) or C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> to give the title glass having visible light transmissivity 5-35%, sun light transmissivity 15-45%, and visible light diffusive transmissivity ≤2%.

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